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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Water-Thinnable Two-Component Coating Composition

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Notice: This application is as filed and may therefore contain an
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Abstract

Water-thinnable two-component coating composition

A water-thinnable two-component coating composition, comprising

- 1) a polyisocyanate component and
- 2) a polyester resin which is composed of the starting components (a), (b), (c), (d) and (e) or their ester-forming derivatives, the ratio of the sum of the hydroxyl equivalents to the sum of the carboxyl equivalents in the reactants being between 1:0.5 and 1:2.0, where
 - (a) is at least one dicarboxylic acid which is not a sulfo monomer,
 - (b) is 0 to 15 mol% of at least one difunctional sulfo or phosphono monomer, whose functional groups are carboxyl and/or hydroxyl groups, with at least one sulfonate or phosphonate group,
 - (c) is at least one glycol,
 - (d) is 0 to 40 mol% of a higher-functional compound (functionality >2), whose functional groups are hydroxyl and/or carboxyl groups, and
 - (e) is 0 to 20 mol% of a monofunctional carboxylic acid,

the amounts of free hydroxyl groups being between 30 and 350 milliequivalents of OH/100 g and the content of free neutralized and/or neutralizable acid groups being between 5 and 350 meq/100 g.

These coating compositions are suitable in particular for the preparation of primers, fillers, topcoats and one-coat finishes.

Water-thinnable two-component coating composition

5 The invention relates to a water-thinnable two-component coating composition based on polyester resins, to a process for its preparation and to its use as a coating.

10 The switch from conventional coatings to water-thinnable systems is proceeding at full pace. In one-component systems, in particular, the replacement of conventional binders by aqueous binders has already reached an advanced stage.

15 What is proving difficult is the use of conventional binders in high-quality two-component systems. Especially in the case of chemically crosslinking polyurethane coatings, which due to their outstanding properties are of great importance in the coatings sector, it has so far not been possible to dispense with organic solvents. The use of aqueous binders appeared problematic in that the polyisocyanate compounds employed as curing agents react 20 with water with the formation of N-substituted polyurea compounds and the elimination of carbon dioxide.

25 It is known from EP 0 358 979 that specific polyhydroxy polyacrylates are capable of emulsifying polyisocyanate curing agents in water and curing to give crosslinking films.

EP 0 469 389 describes a two-component coating composition comprising an aqueous dispersion of a polyurethane and a water-dispersible polyisocyanate, which cures at room temperature.

30 Surprisingly, it has now been found that selected water-thinnable polyester resins described in greater detail

below are particularly favorable for combining unblocked polyisocyanate curing agents, having an excellent emulsifier effect for them.

5 The invention therefore provides a water-thinnable two-component coating composition comprising

- 1) a polyisocyanate component composed of one or more organic polyisocyanates, and
- 2) a polyester resin which is composed of the starting components (a), (b), (c), (d) and (e) or their 10 ester-forming derivatives, the sum of the reactants being 100 mol% and the ratio of the sum of the hydroxyl equivalents to the sum of the carboxyl equivalents in the reactants being between 1:0.5 and 1:2.0.

15 The polyester resin is composed of

- (a) at least one dicarboxylic acid that is not a sulfo monomer,
- (b) 0 to 15 mol%, preferably 1 to 6 mol%, of at least one difunctional sulfo or phosphono monomer, whose functional groups are carboxyl and/or hydroxyl groups, with at least one sulfonate or phosphonate group,
- (c) at least one glycol,
- (d) 0 to 40 mol%, preferably 8 to 20 mol%, of a 25 higher-functional compound (functionality >2), whose functional groups are hydroxyl and/or carboxyl groups, and
- (e) 0 to 20 mol% of a monofunctional carboxylic acid.

30 In this polyester resin the quantity of free hydroxyl groups is between 30 and 350 milliequivalents of OH/100 g, preferably between 100 and 250 meq of OH/100 g, and the content of free neutralized and/or neutralizable acid groups, in particular sulfonic, phosphonic and 35 carboxylic acid groups, is between 5 and 350 meq/100 g, preferably between 10 and 120 meq/100 g.

The invention further relates to a process for the preparation of this coating composition and to its use as a coating.

5 The polyisocyanate component 1) is any desired organic polyisocyanate, preferably a diisocyanate having aliphatically, cycloaliphatically, araliphatically and/or aromatically attached free isocyanate groups which is liquid at room temperature. The polyisocyanate component 1) generally has a viscosity of 50 to 20,000 mPa.s at 10 23°C. It is particularly preferably a polyisocyanate or polyisocyanate mixture containing only aliphatically and/or cycloaliphatically attached isocyanate groups and having an (average) NCO functionality of between 2.0 and 5.0.

15 The polyisocyanates may if required be used as a mixture with small amounts of inert solvents, in order to reduce the viscosity to a value within the stated ranges. However, the amount of such solvents is preferably calculated so that, in the coatings according to the 20 invention which are ultimately obtained, not more than 30% by weight of solvent is present, the calculation including the solvent which may still be present in the polyester resin dispersions or solutions. Examples of suitable solvents for the polyisocyanates are aromatic 25 hydrocarbons, such as solvent naphtha or other solvents, such as butylglycol, N-methylpyrrolidone, methoxypropanol, isopropanol, butanol and acetone.

30 The polyisocyanates, preferably diisocyanates, are compounds known in the polyurethane or coatings sector, such as aliphatic, cycloaliphatic or aromatic diisocyanates. They are preferably of the formula $Q(NCO)_2$, where Q is a hydrocarbon radical having 4 to 40 carbon atoms, in particular 4 to 20 carbon atoms, and is preferably an aliphatic hydrocarbon radical having 4 to 12 35 carbon atoms, a cycloaliphatic hydrocarbon radical having 6 to 15 carbon atoms, an aromatic hydrocarbon radical

having 6 to 15 carbon atoms or an araliphatic hydrocarbon radical having 7 to 15 carbon atoms. Examples of such diisocyanates to be employed with preference are tetramethylene diisocyanate, hexamethylene diisocyanate, 5 dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), 4,4'-diisocyanato-dicyclohexylmethane, 4,4'-diisocyanato-2,2-dicyclohexylpropane, 1,4-diisocyanatobenzene, 2,4- or 2,6-diisocyanatotoluene or mixtures of these isomers, 4,4'- or 2,4'-diisocyanatodiphenylmethane, 4,4'-diisocyanato-2,2-diphenylpropane, p-xylylene diisocyanate and a,a,a',a'-tetramethyl-*m*- or -*p*-xylylene diisocyanate, or mixtures composed of these compounds.

15 In addition to these simple polyisocyanates those containing heteroatoms in the radical linking the isocyanate groups are also suitable. Examples of these polyisocyanates are those containing carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups, 20 acylated urea groups or biuret groups. With regard to further suitable polyisocyanates, reference is made by way of example to German Offenlegungsschrift 29 28 552.

Highly suitable examples are coating-grade polyisocyanates based on hexamethylene diisocyanate or on 25 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and/or bis(isocyanatocyclohexyl)methane, in particular those based exclusively on hexamethylene diisocyanate. Coating-grade polyisocyanates based on these diisocyanates are to be understood as meaning the 30 derivatives of these diisocyanates which have biuret, urethane, uretdione and/or isocyanurate groups and are known per se, which after their preparation have, if required, been freed in a known manner, preferably by distillation, from excess starting diisocyanate down to 35 a residual content of less than 0.5% by weight. The preferred aliphatic polyisocyanates to be used in accordance with the invention include the polyisocyanates

which are based on hexamethylene diisocyanate, fulfill the abovementioned criteria and contain biuret groups, as can be obtained by, for example, the processes of US Patents 3,124,605, 3,358,010, 3,903,126, 3,903,127 or 5 3,976,622 and which comprise mixtures of N,N,N-tris(6-isocyanatohexyl)biuret with minor amounts of its higher homologs, and the cyclic trimers of hexamethylene diisocyanate which fulfill the above criteria, as can be obtained in accordance with 10 US-A-4,324,879, which essentially consist of N,N,N-tris-(6-isocyanatohexyl) isocyanurate in a mixture with minor amounts of its higher homologs. Of particular preference are mixtures of polyisocyanates based on hexamethylene diisocyanate which contain uretdione and/or isocyanurate 15 groups and which fulfill the above criteria, as are formed by the catalytic oligomerization of hexamethylene diisocyanate using trialkyl phosphanes. The last-mentioned mixtures particularly preferably have a viscosity of 50 to 20,000 mPa.s at 23°C and an NCO 20 functionality of between 2.0 and 5.0.

Also suitable are hydrophilic polyisocyanates which are stabilized in the aqueous phase by a sufficient number of anionic groups and/or by terminal or lateral polyether chains, as are described in EP 0 469 389, EP 0 061 628 25 and EP 0 206 059.

The aromatic polyisocyanates which are also suitable in accordance with the invention but are less preferred are in particular coating-grade polyisocyanates based on 2,4-diisocyanatotoluene or technical-grade mixtures 30 thereof with 2,6-diisocyanatotoluene or based on 4,4'-diisocyanatodiphenylmethane or its mixtures with its isomers and/or higher homologs. Examples of aromatic coating polyisocyanates of this type are the isocyanates containing urethane groups, as are obtained by reaction 35 of excess amounts of 2,4-diisocyanatotoluene with polyhydric alcohols such as trimethylolpropane and the possible subsequent distillative removal of the unreacted

diisocyanate excess. Examples of further aromatic coating polyisocyanates are the trimers of the monomeric diisocyanates mentioned by way of example, i.e. the corresponding isocyanato-isocyanurates which, following 5 their preparation, may have been freed from excess monomeric diisocyanates, preferably by distillation.

It is of course also possible in principle to use unmodified polyisocyanates of the type mentioned by way of example, provided they conform to the statements made 10 regarding viscosity.

The polyisocyanate component 1) can also comprise any desired mixtures of the polyisocyanates mentioned.

The polyester resin (2) is, as described above, composed of the starting components (a), (b), (c), (d) and (e) or 15 their ester-forming derivatives.

The terms higher-functional, multifunctional or poly-functional as used herein refer to compounds having more than two reactive hydroxyl and/or carboxyl groups; the term glycol refers to a compound having two and the term 20 polyol to a compound having more than two hydroxyl substituents.

The dicarboxylic acid component (a) of the polyester comprises aromatic, cycloaliphatic or aliphatic saturated or unsaturated dicarboxylic acids and dimeric fatty acids 25 or mixtures of two or more of these dicarboxylic acids. Examples of these dicarboxylic acids are oxalic, malonic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, maleic and intaconic acid, 1,3-cyclopentanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexane-30 dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, phthalic, terephthalic and isophthalic acid, 2,5-norbornanedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, biphenyldicarboxylic acid, 4,4'-sulfonyldibenzoic acid and 2,5-naphthalene-

dicarboxylic acid, and their esters and anhydrides.

Preferred dicarboxylic acid components (a) are phthalic, isophthalic and terephthalic acid, phthalic anhydride, adipic acid, succinic acid and its anhydride, dimeric 5 fatty acids, sebacic and azelaic acid, 1,3-cyclohexanedi-carboxylic acid and glutaric acid and esters thereof.

Component (b) of the polyester is a difunctional aromatic, cycloaliphatic or aliphatic compound having reactive carboxyl and/or hydroxyl groups which also has 10 a group $-\text{SO}_3\text{X}-$ or $-\text{P}(\text{O})(\text{OX})_2-$, where X is hydrogen or a metal ion such as Na^+ , Li^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} or a nitrogen-containing cation of aliphatic, cycloaliphatic or aromatic compounds, such as ammonia, triethylamine, dimethylethanolamine, diethanolamine, triethanolamine and 15 pyridine.

The groups $-\text{SO}_3\text{X}-$ or $-\text{P}(\text{O})(\text{OX})_2-$ can be attached to an aromatic nucleus such as phenyl, naphthyl, biphenylyl nucleus, methylenediphenyl or anthracenyl. Hydroxy- and carboxyarylsulfonic acids are preferred.

20 Examples of component (b) are sulfoisophthalic acid, sulfoterephthalic acid, sulfophthalic acid, sulfo-salicylic acid, sulfosuccinic acid and esters thereof. Particular preference is given to the Na salts of sulfoisophthalic acid, sulfoisophthalic acid dimethyl 25 ester, sulfosalicylic acid and sulfosuccinic acid.

The proportion of component (b) is 0 to 15 mol%, particularly preferably up to 6 mol%.

30 The glycol component (c) may comprise low molecular weight aliphatic, cycloaliphatic or aromatic glycols, polyhydroxy polyethers or polycarbonate-polyols. Examples of low molecular weight glycols are ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol,

1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-
 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclo-
 hexanedimethanol, 1,4-cyclohexanedimethanol, perhydro-
 bisphenol A and p-xylylenediol, and 2-ethyl-2-butyl-
 5 propanediol.

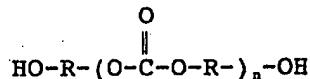
Suitable polyhydroxy polyethers are compounds of the formula



in which

10 R is hydrogen or a low alkyl radical which may have various substituents,
 n is a number from 2 to 6 and
 m is a number from 6 to 120.
 Examples are poly(oxytetramethylene) glycols, poly(oxyethylene) glycols and poly(oxypropylene) glycols. The preferred polyhydroxy polyethers are poly(oxypropylene) glycols having a molecular weight in the range from 400 to 5000.

20 The polycarbonate-polyols or polycarbonate-diols are compounds of the formula



25 in which R is an alkylene radical. These OH-functional polycarbonates can be prepared by reacting polyols such as propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, diethylene glycol, triethylene glycol, 1,4-bishydroxy-methylcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, neopentylglycol, trimethylolpropane and pentaerythritol
 30 with dicarbonates such as dimethyl, diethyl or diphenyl carbonate or phosgene. Mixtures of these polyols can also be employed.

The proportion of component (c) should be calculated so

as to conform to the ratio of hydroxyl equivalents to carboxyl equivalents which was indicated initially.

The higher-functional component (d) which preferably contains 3 to 6 hydroxyl and/or carboxyl groups preferably comprises trimethylolpropane, trimethylolethane, glycerol, ditrimethylolpropane, pentaerythritol, dipentaerythritol, bishydroxyalkanecarboxylic acids, such as dimethylolpropionic acid, trimellitic anhydride and polyanhydrides as described in DE 28 11 913 or mixtures of two or more of these compounds, the proportion of the higher-functional component (d) being preferably 5 to 10 mol%, in particular 8 to 20 mol%.

The monofunctional carboxylic acids (e) are primarily fatty acids such as capric acid, lauric acid, stearic acid and palmitic acid, but it is also possible to employ branched carboxylic acids, such as isovaleric acid and isooctanoic acid.

The number-average molecular weight of the polyester resin, determined experimentally using gel permeation chromatography, may lie between 500 and 4000, and is preferably from 1000 to 3500.

The glass transition temperature of the polyesters is preferably between -60°C and 100°C.

In order, if desired, to achieve as far as possible a quantitative cocondensation of the sulfo or phosphono monomer, it may be necessary to carry out the synthesis of the described polyesters in a multistage process. For this purpose all of the hydroxy-functional components are initially reacted in the presence of catalysts with the sulfo or phosphono monomers and, if appropriate, with carboxylic acid-containing components in such a way that, in the condensation, 95% of the quantity of distillate calculated for quantitative conversion is obtained. The aliphatic carboxylic acid components, if appropriate, are

then reacted, the condensation being continued up to the desired content of carboxylic acid equivalents.

When using a bishydroxyalkanecarboxylic acid, an OH-functional polyester is first prepared which is then subjected to a condensation reaction with the bishydroxy-alkanecarboxylic acid and a further dicarboxylic acid to give the desired polyester.

If polycarboxylic anhydrides are used to introduce the anionic groups, then an OH-functional polyester is reacted with the anhydride to give the half-ester, and condensation is then continued up to the desired acid number.

The reaction takes place at temperatures between 140°C and 240°C, preferably between 160°C and 220°C. To avoid losses of glycol, the condensate is distilled using a distillation column. Suitable catalysts are preferably organometallic compounds, in particular compounds containing zinc, tin or titanium, for example zinc acetate, dibutyltin oxide or tetrabutyl titanate. The amount of catalyst is preferably 0.1 to 1.5% by weight of the total batch amount.

The acid groups can be introduced via the individual components into the polyester already in neutralized form; where free acid groups are present in the polyester, they can if desired be neutralized with aqueous solutions of alkali metal hydroxides or with amines, for example with trimethylamine, triethylamine, dimethyl-aniline, diethylaniline, triphenylamine, dimethylethanol-amine, aminomethylpropanol, dimethylisopropanolamine or with ammonia.

The polyester can be isolated in bulk, but it is preferable to prepare a 50 to 95% solution in a water-miscible organic solvent. Suitable solvents in this respect are preferably oxygenated solvents such as alcohols, ketones,

esters and ethers, for example ethanol, n-propanol, isopropanol, isobutanol, butyl acetate and butylglycol, or nitrogen-containing solvents such as N-methylpyrrolidone. The viscosity of these solutions is preferably 5 between 0.5 and 40 Pa.s at 60°C.

This solution is then used to prepare the polyester dispersion, so that amounts of 15 to 65% by weight of polyester, 0 to 30% by weight of organic solvents and 10 35 to 85% by weight of water are present in the dispersions. The resulting pH is 2 to 8.5, preferably 4.0 to 8.0.

The content of polyester resin in the aqueous coating composition is in general 5 to 40% by weight, preferably 15 to 30% by weight, based on the overall aqueous coating 15 composition.

In addition to the polyester resin, the aqueous coating composition can also contain, as binders, up to 60% by weight, preferably up to 30% by weight, based on the polyester resin, of other oligomeric or polymeric 20 materials, such as crosslinking, water-soluble or water-dispersible phenolic resins, polyurethane resins, epoxy resins or acrylic resins, etc., as described for example in European Offenlegungsschrift 89 497.

To prepare the ready-to-use coatings the polyisocyanate 25 component 1) is emulsified in the aqueous dispersion/solution of the polyester resin 2), the dissolved or dispersed polyester resin adopting the function of an emulsifier for the added polyisocyanate. This is true in particular for the preferred case in 30 which polyisocyanates are used which are not hydrophilically modified. It is also possible to use as polyisocyanate component 1) hydrophilic-modified polyisocyanates which, due to the incorporated ionic or nonionic hydrophilic centres, are autodispersible.

Mixing can be carried out by simply stirring the components together at room temperature. The amount of polyisocyanate component is preferably calculated so as to result in an NCO/OH equivalent ratio, based on the 5 isocyanate groups of component 1) and the alcoholic hydroxyl groups of component 2), of 0.5:1 to 5:1, in particular 0.8:1 to 3:1.

Prior to the addition of the polyisocyanate component, the auxiliaries and additives customary in coatings 10 technology can be incorporated into the polyester resin 2), i.e. the dispersion or solution of the polymers. These include for example antifoams, leveling assistants, pigments and pigment dispersants.

The resulting coatings according to the invention are 15 suitable for practically all areas of application which currently employ solvent-containing, solvent-free or other types of aqueous paint and coating systems having an enhanced range of properties.

They are preferably used for topcoats and one-coat 20 finishes, in which case the substrates to be coated may be, for example, metal, mineral construction materials such as limestone, cement or gypsum, fiber-cement construction materials, concrete, wood or timber materials, paper, asphalt, bitumen, plastics of various 25 kinds, textiles or leather. The metallic substrates are preferably in all cases automobiles.

Another preferred use is as a primer or surfacer, in 30 which case the substrates to be coated may be, for example, metal, mineral construction materials such as limestone, cement or gypsum, fiber-cement construction materials, concrete, wood or timber materials, paper, asphalt, bitumen, textiles or leather. The metallic substrates are again preferably automobiles.

Examples:

The polyester synthesis is carried out in a 4 l four-neck flask fitted with a packed column (column tube: 30 mm diameter, 2000 mm length; packing: glass rings of 6 mm diameter and 6 mm length) and a descending bridge-shaped distillation head, with temperature sensing of the reacting material under a protective gas atmosphere (protective gas feed, nitrogen). If low-boiling alcohols, especially methanol, are distilled off as condensate, the receiver should be cooled using an ice bath. The abbreviations used below are explained on page 17.

Polyester 1

Initial amounts as in Table 1

Melt neopentylglycol and trimethylolpropane, add IPA and 15 1.5 g of dibutyltin oxide, heat so that the overhead temperature does not exceed 100°C, subject the mixture to condensation at 190°C to 200°C until the content of acid groups is 10 meq of COOH/100 g.

Cool to 140°C, add ADPA and DMPA, heat so that the 20 overhead temperature does not exceed 100°C, subject the mixture to condensation at temperatures of up to 200°C until a value of 64 meq of COOH/100 g is reached. Then cool to 80°C, add 62.2 g of dimethylethanolamine and 25 290 g of N-methylpyrrolidone and disperse in 2818 g of water.

Polyester 2

Initial amounts as in Table 1

Melt the hydroxyl group-containing reactants, add 5-SIP-Na, TPA and 1.5 g of dibutyltin oxide, heat so that 30 the overhead temperature does not exceed 100°C, subject the mixture to condensation at 185°C to 195°C until 135 g of distillate are obtained.

Cool to 120°C, add IPA and 1.0 g of dibutyltin oxide, heat so that the overhead temperature does not exceed 35 100°C, subject the mixture to condensation at temper-

atures of up to 190°C until the content of free carboxyl groups is 55 meq of COOH/100 g, then continue condensation at 180°C to 200°C and 100 mbar until a value of 7 meq of COOH/100 g is reached.

5 720 g of N-methylpyrrolidone are added at 140°C and the batch is then dispersed with 4680 g of water.

Polyester 3

Initial amounts as in Table 1

10 Melt neopentylglycol and trimethylolpropane, add TPA, IPA and 1.5 g of dibutyltin oxide, heat so that the overhead temperature does not exceed 100°C, subject the mixture to condensation at 190°C to 200°C until the content of acid groups is 10 meq of COOH/100 g.

15 Cool to 140°C, add TMAA and stir at this temperature until a value of 71 meq of COOH/100 g is reached. Then cool to 80°C, add 175 g of N-methylpyrrolidone and 80 g of dimethylethanolamine, and disperse in 1800 g of water.

Polyester 4

Initial amounts as in Table 1

20 Melt neopentylglycol and trimethylolpropane, add TPA, IPA, LA and 2.5 g of dibutyltin oxide, heat so that the overhead temperature does not exceed 100°C, subject the mixture to condensation at 190°C to 200°C until the content of acid groups is 10 meq of COOH/100 g.

25 Cool to 140°C, add ADPA and DMPA, heat so that the overhead temperature does not exceed 100°C, subject the mixture to condensation at temperatures of up to 200°C until a value of 56 meq of COOH/100 g is reached. Then cool to 80°C, add 300 g of N-methylpyrrolidone and 70 g of dimethylethanolamine, and disperse in 2430 g of water.

Table 1 (* see over)

Table 1: Polyesters

		Components										
		IPA	TPA	ADPA	5-SIP-Na	IA	TMAA	DMPA	NPG	EG	TMP	BEG
Poly- ester 1	Initial amount (g)	260	360	400	/	/	/	150	520	/	200	/
	mol	1.56	2.17	2.74	/	/	/	1.12	4.99	/	1.49	/
	mol%	11.1	15.4	19.5	/	/	/	7.9	35.5	/	10.3	/
Poly- ester 2	Initial amount (g)	955	908	/	110	/	/	1075	220	/	/	/
	mol	5.75	5.47	/	0.41	/	/	/	10.32	3.54	/	/
	mol%	22.5	21.5	/	1.6	/	/	/	40.5	13.9	/	/
Poly- ester 3	Initial amount (g)	332	71	150	/	/	100	/	320	/	120	80
	mol	2.0	0.43	1.03	/	/	0.52	/	3.07	/	0.89	0.23
	mol%	24.5	5.3	12.6	/	/	6.4	/	37.6	/	10.9	2.8
Poly- ester 4	Initial amount (g)	260	300	450	/	100	/	150	520	/	220	/
	mol	1.56	1.81	3.08	/	0.5	/	1.12	4.99	/	1.64	/
	mol%	10.6	12.3	20.9	/	3.4	/	7.6	33.9	/	11.2	/

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Continued:

	Ratio OH:COOH with ref. to starting contents	meq (COOH)/100 g	meq (OH)/100 g	meq (SO ₃ Na)/100 g
Polyester 1:	1.215	64	203	/
Polyester 2:	1.195	7	50	14
Polyester 3:	1.35	71	285	/
Polyester 4:	1.18	56	196	/

Key:	IPA	= isophthalic acid
	TPA	= terephthalic acid
	ADPA	= adipic acid
5	5-SIP-Na	= 5-sulfoisophthalic acid Na salt
	NPG	= neopentylglycol
	TMP	= trimethylolpropane
	DMPA	= dimethylolpropionic acid
	EG	= ethylene glycol
10	LA	= lauric acid
	TMAA	= trimellitic anhydride
	PEG	= polyethylene glycol

2-Component primer

The dispersion batch is prepared by mixing 65.8 parts by weight of the polyester (1), (2), (3) or (4) having a solids content of 38% by weight with 0.2 part by weight of a commercially available silicone-free antifoam (Additol VXW 4973 from Hoechst AG), 0.3 part by weight of a commercially available wetting and dispersing auxiliary (Additol XL 250 from Hoechst AG) and 0.4 part by weight of a commercially available leveling agent (Additol XW 390 from Hoechst AG). After simply stirring, 14.0 parts by weight of titanium dioxide (Kronos 2310 from Kronos-Titan GmbH), 11.0 parts by weight of a barium sulfate (Blanc fixe micro from Sachtleben GmbH), 3.7 parts by weight of a talc (Naintsch E 7 from Naintsch Mineralwerke GmbH) and 0.1 part by weight of a carbon black (Flammruss 101 from Degussa AG) are added to the batch, which is dispersed for about 30 minutes in a dissolver at a speed of 6000 rpm.

A variety of polyisocyanates can be employed as the curing component, for example (I) Basonat FDS 3425 from BASF AG, (II) Desmodur VPLS 2550, (III) Desmodur N 3300 and (IV) Desmodur N 100 from Bayer AG.

35 The dispersion batch was then mixed with 12.5 parts by weight of a suitable polyisocyanate which has, if

appropriate, been previously diluted with methoxypropyl acetate; the composition of the batch in accordance with the invention is as follows:

	Example A	Example B	Example C	Example D
Binder	1	2	3	4
	25.00	25.00	25.00	25.00
Pigments	28.80	28.80	28.80	28.80
Auxiliaries	0.90	0.90	0.90	0.90
Total solids	54.70	54.70	54.70	54.70
Deionized water	42.05	40.05	42.05	42.05
Organic solvent	3.25	5.25	3.25	3.25
Total	100.00	100.00	100.00	100.00
Polyisocyanate (III) 12.50 (I) 12.50 (II) 12.50 (III) 12.50				
Methoxypropyl acetate	6.25	0.00	0.00	12.50

The ready-to-process batches have a content of organic solvents of only 2.89 to 12.60% by weight. The coatings are applied to the substrate at a wet-film thickness of 150-300 μm (corresponding to a dry-film thickness of 5 25 to 50 μm) and dried for 30 minutes at 80°C in a circulating-air oven.

The cured coating films of Examples A to D can be characterized as follows:

Solvent resistance	Example A	Example B	Example C	Example D
Isopropanol	good-moderate	very good	moderate	moderate
Isopropanol/water (1:1)	good	very good	moderate	moderate
Ethanol	very good-good	very good-good	moderate	moderate
Ethanol/water (1:1)	good	very good	moderate	moderate
Premium-grade gasoline	good	moderate	moderate	moderate

	Example A	Example B	Example C	Example D
Pendulum hardness acc. to DIN 53157	75"-100"	100"-110"	25"-40"	15"-25"
60° Gloss acc. to DIN 67530	50%	43%	88%	73%
Hot-wet test acc. to DIN 50017 SK	good-moderate	good-moderate	good	moderate
Salt spray test acc. to ASTM-B117-69	good	very good-good	very good-good	very good-good
Topcoat appearance	good	good	very good	good
Stone chip: topcoat adhesion penetrations	good good	good good-moderate	good-moderate good	very good very good

2-Component topcoat

The dispersion batch is prepared by mixing 71.1 parts by weight of polyester (1) or (4) having a solids content of 38% by weight with 0.2 part by weight of a commercially available silicone-free antifoam (Additol VXW 4973 from Hoechst AG), 0.3 part by weight of a commercially available wetting and dispersing auxiliary (Additol XL 250 from Hoechst AG) and 0.4 part by weight of a commercially available leveling agent (Additol XW 390

from Hoechst AG). After the simple stirring of the additives together with one another, 24.6 parts by weight of titanium dioxide (Kronos 2310 from Kronos-Titan GmbH) are added to the batch, which is dispersed for about 30 minutes in a dissolver at a speed of 6000 rpm.

A variety of polyisocyanates can be employed as the curing component, for example (I) Basonat FDS 3425 from BASF AG, (II) Desmodur VPLS 2550, (III) Desmodur N 3300 and (IV) Desmodur N 100 from Bayer AG.

10 The dispersion batch was then mixed with 13.4 parts by weight of a suitable polyisocyanate which is, if appropriate, previously diluted with methoxypropyl acetate; the composition of the batch in accordance with the invention is as follows:

	Example A	Example B	Example C	Example D
Binder	1	2	3	4
	25.00	25.00	25.00	25.00
Pigments	28.80	28.80	28.80	28.80
Auxiliaries	0.90	0.90	0.90	0.90
Total solids	54.70	54.70	54.70	54.70
Deionized water	42.05	40.05	42.05	42.05
Organic solvent	3.25	5.25	3.25	3.25
Total	100.00	100.00	100.00	100.00
Polyisocyanate (III)	12.50	(I) 12.50	(II) 12.50	(III) 12.50
Methoxypropyl acetate	6.25	0.00	0.00	12.50

The ready-to-process batches have a content of organic solvents of only 8.5 to 13.3% by weight. The coatings are applied to the substrate at a wet-film thickness of 200-400 μm (corresponding to a dry-film thickness of 5 30 to 60 μm) and dried for 30 minutes at 80°C in a circulating-air oven.

The cured coating films of Examples E and F can be characterized as follows:

Solvent resistance	Example E	Example F
Isopropanol	very good	very good-good
Isopropanol/water (1:1)	very good	very good-good
Ethanol	very good-good	good
Ethanol/water (1:1)	very good	good
Premium-grade gasoline	very good-good	good-moderate

	Example E	Example F
Pendulum hardness acc. to DIN 53157	about 115"	about 145"
60° Gloss acc. to DIN 67530	about 87%	about 87%
Topcoat appearance	good	good
Stone chip: topcoat adhesion penetrations	good good	good very good-good

The cured films from all the examples are tested in accordance with the following test procedures:

Pendulum hardness: in accordance with DIN 53 157

Degree of gloss: in accordance with DIN 67 530,
5 measured at an angle of 60°

Hot-wet test: in accordance with DIN 50 017 SK.
10 After 240 hours with atmospheric humidity of 100% and at a temperature of 40°C, blistering, gloss and the quality of the coating surface were subjectively assessed according to a rating scale (1 = very good, 5 = very poor)

Salt spray test: in accordance with ASTM-B 117-69.
15 After 240 hours in a salt spray atmosphere, blistering and corrosive penetration at the predetermined corrosion points were subjectively assessed according to a rating scale (1 = very good, 5 = very poor)

20 Topcoat appearance: the gloss and surface of the topcoat were subjectively assessed according to a rating scale (1 = very good, 5 = very poor)

25 Stone chip: The stone-chip resistance was tested using a stone chip testing device in accordance with the VDA [German Motor Industry Association] (model 508 from Erichsen). For these tests, in each case 1 kg of scrap steel (angular, 4-5 mm) was projected under compressed-air acceleration (2 bar) on to the test panels. Using sample panels, an assessment was made of the topcoat adhesion (very good = no abrasion, very poor = complete delamination) and of the penetrations down to the
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metal (very good = no penetrations,
very poor = a large number of
penetrations).

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What is claimed is:

5 1. A water-thinnable two-component coating composition, comprising

10 1) a polyisocyanate component composed of one or more organic polyisocyanates, and

2) a polyester resin which is composed of the starting components (a), (b), (c), (d) and (e) or their ester-forming derivatives, the sum of the reactants being 100 mol% and the ratio of the sum of the hydroxyl equivalents to the sum of the carboxyl equivalents in the reactants

15 being between 1:0.5 and 1:2.0, where

(a) is at least one dicarboxylic acid which is not a sulfo monomer,

20 (b) is 0 to 15 mol% of at least one difunctional sulfo or phosphono monomer, whose functional groups are carboxyl and/or hydroxyl groups, with at least one sulfonate or phosphonate group,

(c) is at least one glycol,

25 (d) is 0 to 40 mol% of a higher-functional compound (functionality >2), whose functional groups are hydroxyl and/or carboxyl groups, and

(e) is 0 to 20 mol% of a monofunctional carboxylic acid,

30 the amounts of free hydroxyl groups being between 30 and 350 milliequivalents of OH/100 g, preferably between 100 and 250 meq of OH/100 g, and the content of free neutralized and/or neutralizable acid groups, in particular sulfonic, phosphonic and carboxylic acid groups, being between 5 and 350 meq/100 g, preferably between 9 and 120 meq/100 g.

2. A water-thinnable two-component coating composition as claimed in claim 1, comprising a polyester resin prepared from
 - (a) aliphatic, aromatic or cycloaliphatic dicarboxylic acids,
5
 - (b) hydroxy- and carboxyarylsulfonic acids or salts thereof,
 - (c) aliphatic, aromatic or cycloaliphatic glycols, and
 - 10 (d) compounds containing 3 to 6 hydroxyl groups and/or carboxyl groups.
3. A water-thinnable two-component coating composition as claimed in claim 1, comprising a polyester resin prepared from
 - (a) phthalic, isophthalic and terephthalic acid, phthalic anhydride, adipic acid, sebacic and azelaic acid, 1,3-cyclohexanedicarboxylic acid or glutaric acid and esters thereof,
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 - (b) sulfoisophthalic acid, sulfoterephthalic acid, sulfophthalic acid, sulfosalicylic acid and esters or salts thereof,
 - (c) ethylene glycol, 1,2-propanediol, 1,3-butanediol, 1,6-hexanediol or perhydrobisphenol A,
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 - (d) trimethylolpropane, trimethylolethane, glycerol, ditrimethylolpropane, pentaerythritol, dipentaerythritol, dimethylolpropionic acid or trimellitic anhydride.
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4. A water-thinnable two-component coating composition as claimed in claim 1, comprising a polyester resin composed of 1 to 6 mol% of component (b) and 8 to 30 20 mol% of component (d).
5. The use of a water-thinnable two-component coating composition as claimed in claims 1 to 4 for the preparation of topcoats and one-coat finishes.
- 35 6. The use of a water-thinnable two-component coating

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composition as claimed in claims 1 to 4 for the preparation of primers or fillers.

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